PATENT ABSTRACTS OF JAPAN

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(54) PRODUCTION OF HYDROGEN STORAGE ALLOY, ALLOY THEREOF AND ELECTRODE USING THE ALLOY

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a hydrogen storage alloy having low oxygen concn. from a vanadium base alloy having high oxygen concn. in a low cost by heating and melting the vanadium base alloy raw material together with at least one kind of deoxidizer.

SOLUTION: The vanadium base alloy raw material (about 2000-20000 ppm oxygen content) in low cost obtaining a part or all thereof with a thermit reduction process is heated and melted together with at least one kind of the deoxidizer. As the deoxidizer, it is desirable to use Ca-Ni base alloy (CaNi5, or the like), Mg-Ni base alloy (Mg2Ni, or the like), La (or Ce)-Ni base alloy (LaNi, CeNi or the like). Further, the additional quntity of the deoxidizer is made to about 1-3 times of the reduction equivalent of oxygen contained in the vanadium base alloy raw material, and the melting is executed under inert gas atmosphere or vacuum condition by using an arc melting furnace. By this method, in the melting process, the oxygen contained in the vanadium base alloy raw material is reacted with the deoxidizer and discharged to out of the alloy system as the oxide.

LEGAL STATUS

[Date of request for examination]　　　　　31.10.1997

[Date of sending the examiner's decision of rejection]　12.01.2000

[Kind of final disposal of application other than the
examiner's decision of rejection or application
converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of
rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

(54)【発明の名称】 水素吸蔵合金の製造方法、その合金及びその合金を用いた電極

(57)【要約】
【課題】特に低コストで得られる高酸素濃度のバナジウム又はその合金を用いて、優れた電極特性を発揮できる水素吸蔵合金を製造することを主な目的とする。
【解決手段】バナジウム基合金からなる水素吸蔵合金の製造方法であって、バナジウム系合金原料を脱酸剤の少なくとも1種とともに加熱溶解することを特徴とする水素吸蔵合金の製造方法、その製造方法により得られた水素吸蔵合金及びその合金を用いた水素化物電極。

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【特許請求の範囲】

【請求項1】バナジウム基合金からなる水素吸蔵合金の製造方法であって、バナジウム系合金原料を脱酸剤の少なくとも1種とともに加熱溶解することを特徴とする水素吸蔵合金の製造方法。

【請求項2】バナジウム系合金原料の酸素含有量が2000〜20000ppmである請求項1記載の製造方法。

【請求項3】バナジウム系合金原料の一部又は全部が、テルミット還元法によって得られたものである請求項1記載の製造方法。

【請求項4】脱酸剤が、バナジウム系合金原料中に含有される酸素と選択的に反応し、酸化物として合金系外に排出されるものである請求項1記載の製造方法。

【請求項5】脱酸剤が、Ca、Mg及び希土類元素ならびにこれらの合金の少なくも1種である請求項4記載の製造方法。

【請求項6】脱酸剤が、Ca、Mg及び希土類元素の少なくも1種とニッケルとの合金である請求項5記載の製造方法。

【請求項7】脱酸剤が、Ca−Ni系合金の少なくとも1種である請求項6記載の製造方法。

【請求項8】脱酸剤が、Mg−Ni系合金の少なくとも1種である請求項6記載の製造方法。

【請求項9】脱酸剤が、希土類元素−Ni系合金の少なくとも1種である請求項6記載の製造方法。

【請求項10】請求項1ないし9のいずれかに記載の方法によって得られたバナジウム基合金であって、添加した脱酸剤の少なくとも一部が当該合金中に固溶していることを特徴とする水素吸蔵合金。

【請求項11】脱酸剤の固溶量が0.5〜2at.％である請求項10に記載の水素吸蔵合金。

【請求項12】バナジウム基合金であって、V−Ti系固溶体合金からなる母相中にTiNi相を主成分とする第二相が三次元網目骨格を形成して存在し、かつ、母相及び第二相の少なくとも一方に脱酸剤が固溶していることを特徴とする請求項10又は11に記載の水素吸蔵合金。

【請求項13】バナジウム基合金であって、V−Ti系固溶体合金からなる母相中にTi−Ni−V系AB$_2$型ラーベス相を主相とする第二相が三次元網目骨格を形成して存在し、かつ、母相及び第二相の少なくとも一方に脱酸剤が固溶していることを特徴とする請求項10又は11に記載の水素吸蔵合金。

【請求項14】請求項10ないし13のいずれかに記載の水素吸蔵合金を用いた水素化物電極。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、バナジウム基合金からなる水素吸蔵合金の製造方法に関する。さらには、

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その製造方法によって得られる水素吸蔵合金及びその合金を用いた水素化物電極に関する。

【0002】

【従来技術】従来における水素吸蔵合金としては、V−Ti系固溶体合金からなる母相中に第二相として①TiNi相を主成分とする第二相又は②Ti−Ni−V系AB$_2$型ラーベス相を主相とする第二相が三次元網目骨格を形成している合金が知られている（特開平7−268513号、特開平7−268514号）。

【0003】これらの合金をアルカリ二次電池の負極活物質として用いる場合は、第二相である三次元網目骨格の存在により次のような効果が得られる。すなわち、第二相は母相を包み込む状態で存在しているため、水素吸蔵に伴う微粉化を大幅に抑制できる。また、第二相が母相に対する保護膜となって水素吸蔵合金の主成分であるバナジウムの溶解を抑制又は防止できる。そして、これらによって、充放電の繰り返し、放置等に対する耐久性の向上を図ることができる。

【0004】さらに、第二相は、反応触媒として、あるいは合金の水素化・脱水素化反応で水素吸蔵合金がやりとりする電子の伝導体（集電体）として機能するので放電時の反応速度を増大させることができる。

【0005】そして、これら水素吸蔵合金は、通常は原料金属を所定の組成となるように秤量した後、例えばアーク溶解法、高周波誘導加熱法等の公知の溶解方法でこれらを加熱溶解させ、冷却凝固することにより製造されている。

【0006】ところで、バナジウム基合金からなる水素吸蔵合金において、バナジウムが酸素を含有した場合には、水素吸蔵量が著しく減少することが報告されている（J.J.Rcilly and R.H.Wiswall Jr.; BNL-16546(Brookhaven National Laboratory,Upton,N.Y.,1972)）。このため、水素吸蔵合金において、バナジウム固溶体相に含有される酸素量はできるだけ低く抑える必要がある。

【0007】従来、鉄鋼添加用の安価なバナジウム系合金の製造には、テルミットプロセス（テルミット還元法）が広く利用されている。これは、バナジウム酸化物の粉末とアルミニウム等の還元材金属を混合し、混合物を耐火ルツボ中で加熱して還元反応を進行させ、さらに反応の自己発熱を利用して反応を完結させる。還元材金属として、例えばアルミニウムがよく用いられており、その場合の還元反応は以下のようになる。

【0008】$3V_2O_5 + 10Al \rightarrow 6V + 5Al_2O_3$
還元反応後において、これらの還元材金属の酸化物は、比重が小さいため耐火ルツボの上部に浮上し、還元されて生成した金属バナジウム（以下、単に「バナジウム」という）は底部に堆積することにより両者は分離される。

【0009】

【発明が解決しようとする課題】しかしながら、この方

法により得られるバナジウムは、反応時間が短いために十分に還元されていないことが多く、また還元反応により生成した酸化物がバナジウム中にも残留しやすく、その結果としてバナジウム中に通常10000〜20000ppmという高濃度の酸素が一般に存在することとなる。このバナジウムを用い、他の元素とともに加熱溶解して得られた水素吸蔵合金も、同レベルの酸素を含んでいる。しかも、含有される酸素は、水素吸蔵合金における水素占有サイトを占めるため、大きな水素吸蔵量は期待できず、水素吸蔵合金として十分な機能を発揮することができない。

【0010】従って、本発明は、特に低コストで得られる高酸素濃度のバナジウム又はその合金を用いて、優れた電極特性を発揮できる水素吸蔵合金を製造することを主な目的とする。

【0011】

【課題を解決するための手段】本発明者は、上記の従来技術の問題に鑑み、鋭意研究を重ねた結果、特定の製造方法により水素吸蔵合金を製造する場合には上記目的を達成できることを見出し、ついに本発明を完成するに至った。

【0012】すなわち、本発明は、バナジウム基合金からなる水素吸蔵合金の製造方法であって、バナジウム系合金を脱酸剤の少なくとも1種とともに加熱溶解することを特徴とする水素吸蔵合金の製造方法に係るものである。

【0013】また、本発明は、上記製造方法によって得られたバナジウム基合金であって、特に、①V−Ti系固溶体合金からなる母相中にTiNi相を主成分とする第二相が三次元網目骨格を形成して存在し、かつ、母相及び第二相の少なくとも一方に脱酸剤が固溶していることを特徴とする水素吸蔵合金、あるいは②V−Ti系固溶体合金からなる母相中にTi−Ni−V系AB2型ラーベス相を主相とする第二相が三次元網目骨格を形成して存在し、かつ、母相及び第二相の少なくとも一方に脱酸剤が固溶していることを特徴とする水素吸蔵合金に係るものである。

【0014】さらに、本発明は、上記製造方法によって得られた水素吸蔵合金を用いた水素化物電極にも係るものである。

【0015】

【発明の実施の形態】本発明で用いるバナジウム系合金原料としては、バナジウムを含むものである限り特に制限されない。例えば、バナジウム又はバナジウム合金と他の金属、合金等との混合物を用いることができる。また、例えば金属成分の組成が所望の水素吸蔵合金と同じ組成のバナジウム合金をそのまま本発明バナジウム系合金原料として用いることもできる。

【0016】バナジウム又はバナジウム合金と他の金属、合金等との混合物としては、所望の合金組成、合金組織等に応じてチタン原料、ニッケル原料、タンタル原料、コバルト原料、ハフニウム原料、ジルコニウム原料等の金属、合金等をバナジウム又はバナジウム合金に混合したものを用いることができる。

【0017】バナジウム合金としては、例えばフェロバナジウム、ニッケルバナジウム等のバナジウム基合金等が挙げられる。その他にも、バナジウムを含む2元系、3元系、多元系等の合金もそのまま用いることができる。なお、本発明でいう「合金」は、合金のみならず金属間化合物も含む概念である（以下も同様）。

【0018】特に、本発明では、酸素含有量（以下「酸素濃度」ともいう）が2000ppm以上である高酸素濃度のバナジウム系合金原料も有効に用いることができる。すなわち、バナジウム系合金原料中には、通常は2000〜20000ppm程度の酸素が含有されているが、本発明ではこのような高酸素濃度のバナジウム系合金原料からも優れた水素吸蔵合金を製造することができる。高酸素濃度のバナジウム系合金原料は、一般に安価に入手でき、しかも粉砕しやすいので秤量する際の取り扱いが容易である等の点で特に有利である。一方、本発明において、酸素濃度が低いバナジウム系合金原料を使用すればそれだけ優れた特性を発揮する水素吸蔵合金が得られる。なお、本発明におけるppm単位は「mass ppm」を示す（以下も同様）。

【0019】本発明の製造方法では、バナジウム系合金原料の一部又は全部として、例えば精製した酸化バナジウムを出発原料とし、この原料から金属アルミニウムによるテルミット還元法によって得られるバナジウム又はその合金を好適に用いることができる。一般に、テルミット還元法によるバナジウム又はその合金は、酸素が固溶した状態で含まれているか、あるいは$V_{16}O_3$のような化合物として含まれているので、破砕しやすく、また低廉であり、コスト面で有利である。また、テルミット還元法において、還元材金属としてマグネシウム又はカルシウムを用いて不活性ガス中又は真空中で還元されたバナジウム又はその合金を使用することも可能である。

【0020】また、バナジウム系合金原料中に含有される酸素は、どのような形態で含有されていても良い。例えば、前記のように、バナジウム中に固溶して存在しても良く、あるいは酸化物（例えば、$V_{16}O_3$等）として存在していても良い。

【0021】本発明における脱酸剤としては、バナジウム系合金原料中に含有される酸素の少なくとも一部と反応し、その酸素含有量の低減を図ることができる限り制限されない。特に、バナジウム系合金原料中に含有される酸素と選択的に反応し、酸化物として合金系外に排出できるものが好ましい。具体的には、原料中に含まれる酸素と選択的に反応して酸化物を生成し、この酸化物が実質的に水素吸蔵合金の組織外に排出されるような脱酸剤であれば良い。

【００２２】本発明では、Ca、Mg及び希土類元素ならびにこれらの合金の少なくも１種が好ましく、特にCa、Mg及び希土類元素の少なくも１種とニッケルからなる合金がより好ましい。

【００２３】このような合金としては、例えばCa－Ni系合金（$CaNi_5$、$CaNi_2$等）、Ca－Al系合金（$CaAl_2$等）、Mg－Ni系合金（Mg_2Ni、$MgNi_2$等）、Mg－Al系合金（Mg_2Al_3等）、La、Ce等の希土類元素又はその混合物（Mm：ミッシュメタル）とニッケルとの合金（$LaNi$、$CeNi_2$、$MmNi_5$等）、あるいはこれらの混合物又は固溶体（Ca－Mg－La－Ni系合金等）が挙げられる。これら脱酸剤の中でも、特にCa－Ni系合金、Mg－Ni系合金、La（又はCe）－Ni系合金等は、Ca、Mg、La、Ce等の単体を用いる場合に比べて溶解中における反応を制御しやすいという点で好ましい。

【００２４】脱酸剤の添加量は、用いる脱酸剤の種類等に応じて適宜設定することができるが、通常はバナジウム系合金原料中に含有する酸素の還元当量の１～３倍程度、好ましくは１．２～２倍とすれば良い。

【００２５】次いで、これら合金原料を所望の組成となるように秤量し、これら合金原料を加熱溶解（単に「溶解」ともいう）して合金化した後、脱酸剤を投入して再溶解を行う。

【００２６】溶解する方法は、不活性ガス（アルゴン、ヘリウム等）雰囲気下又は真空下であれば特に制限されず、公知の方法に従って加熱溶解すれば良い。溶解は、特に溶湯の温度差をなくすために撹拌しながら行うことが好ましい。このような点において、例えばアーク溶解炉、高周波誘導加熱溶解炉等の公知の溶解装置を好適に用いることができる。なお、アーク溶解炉で溶解する場合は、溶解初期の脱酸剤の揮発を防ぐために、溶解初期の段階では脱酸剤を直接アークに晒さないようにすることが好ましい。高周波誘導加熱溶解炉を用いる場合は、合金溶湯に、脱酸剤を粉末状又は顆粒状（平均粒径１００μm～１０mm程度）として配合することが好ましい。

【００２７】また、溶解では、例えば溶湯をいったん冷却した後、合金塊を反転し、再び溶解するという工程を数回繰り返すことによって、得られる鋳造合金の組織の均質化を図るとともに、合金組織外へ酸化物等の排出を促進することができる。

【００２８】溶解工程では、各元素は液相に変化し、バナジウム系合金原料（特にバナジウム）中に含有されている酸素は脱酸剤と反応して、酸化物として合金系外に排出される。また、未反応の脱酸剤は、合金への固溶量が通常５at.％以下と少なく、固溶できないものは、一般に合金と分離した状態で相を形成する。

【００２９】具体的には、合金中で脱酸剤と反応して生成した酸化物は、例えば鋳造合金塊の表面、粒界（第二相中）等に析出したり、あるいは炉内にスラグとして残る。一方、酸素との反応に寄与しなかった脱酸剤は、合金中に固溶したり、あるいは固溶範囲を超えた分は合金と分離した状態で相を形成することとなる。

【００３０】このように、脱酸剤は、溶解工程中に、酸化物として合金組織外に排出されるので、得られる水素吸蔵合金中には酸化物はほとんど残存していない。特に、水素吸蔵合金における母相には、酸化物は存在せず、実質的にバナジウム固溶体のみから構成される。

【００３１】但し、本発明の効果を妨げない範囲内において（特に、母相の酸素含有量を低減できる限りは）、脱酸剤、酸化物等が水素吸蔵合金のいずれかの箇所に残留していても良い。例えば、脱酸剤が一部合金（母相、粒界等）中に固溶した状態で残留する場合もあるが、この場合も少なくとも合金母相中の酸素含有量が低減できる限り、水素吸蔵合金としての特性向上に寄与し得るので、本発明に包含される。

【００３２】本発明では、加熱溶解した後、冷却を行う。冷却方法は、特に制限されず、例えば炉内又は大気中に放置することによる徐冷凝固、水冷装置に流し込む急冷凝固、回転する銅ロールに滴下する超急冷凝固等により冷却することができる。この場合、冷却速度を制御することによって、母相の結晶粒径、第二相の析出形態等を制御できる。

【００３３】本発明の製造方法では、脱酸剤の使用によって酸素濃度を効果的に低減化できることから、２元系又は多元系のバナジウム基合金からなる水素吸蔵合金の製造に適用でき、また所望の性能（電池）等に応じて種々の第二相を形成させることも可能である。

【００３４】従って、本発明の製造方法においては、添加した脱酸剤の少なくとも一部が固溶したバナジウム基合金を得ることもできる。例えば、以下のV－Ti系固溶体合金からなる水素吸蔵合金を製造することができる。

【００３５】（１）V－Ti系固溶体合金において、V－Ti系固溶体合金からなる母相中にTiNi相を主成分とする第二相が三次元網目骨格を形成して存在する水素吸蔵合金

例えば、合金組成$V_{\alpha}TiNi_{\beta}M_{\gamma}$（但し、MはCr、Mn、Fe、Co、Cu、Nb及びTaの少なくとも１種、$1 \leq \alpha \leq 10$、$0.2 \leq \beta \leq 2$、$0.02 \leq \gamma \leq 0.5$）となるように各原料を配合すれば良い。この場合、TiNi相を主成分とする合金相（第二相）として$TiNi_{\delta}N_{\varepsilon}$（但し、NはV、Cr、Mn、Fe、Co、Cu、Nb及びTaの少なくとも１種、$0.5 \leq \delta \leq 2$、$0.1 \leq \varepsilon \leq 1$）が主に形成される。

【００３６】（２）V－Ti系固溶体合金において、V－Ti系固溶体合金からなる母相中にTi－Ni－V系AB_2型ラーベス相を主相とする合金相が三次元網目骨格を形成して存在する水素吸蔵合金の場合

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① 例えば、合金組成$V_\alpha Ti Ni_\beta A_\gamma M_\delta$（但し、AはZr、Hf及びTaの少なくとも1種、MはCr、Mn、Fe、Co、Cu及びNbの少なくとも1種、$1 \leq \alpha \leq 10$、$0.2 \leq \beta \leq 2$、$0.05 \leq \gamma \leq 1$、$0 < \delta \leq 2$）となるように配合すれば良い。この場合、AB$_2$型ラーベス相を主相とする合金相（第二相）として$Ti_\epsilon A_\zeta Ni_\eta V_\theta M_\iota$（但し、AはZr、Hf及びTaの少なくとも1種、MはCr、Mn、Fe、Co、Cu及びNbの少なくとも1種、$0.1 \leq \epsilon \leq 0.4$、$0.1 \leq \zeta \leq 0.4$、$0.1 \leq \eta \leq 0.6$、$0.1 \leq \theta \leq 0.5$、$0 < \iota \leq 0.2$、かつ、$\epsilon + \zeta + \eta + \theta + \iota = 1$）が主に形成される。

【0037】② 例えば、合金組成$V_\alpha Ti Ni_\beta A_\gamma$（但し、AはZr、Hf及びTaの少なくとも1種、$1 \leq \alpha \leq 10$、$0.2 \leq \beta \leq 2$、$0.05 \leq \gamma \leq 1$）となるように配合すれば良い。この場合、AB$_2$型ラーベス相を主相とする合金相（第二相）として$Ti_\epsilon A_\zeta Ni_\eta V_\theta$（但し、AはZr、Hf及びTaの少なくとも1種、$0.1 \leq \epsilon \leq 0.4$、$0.1 \leq \zeta \leq 0.4$、$0.1 \leq \eta \leq 0.6$、$0.1 \leq \theta \leq 0.5$、かつ、$\epsilon + \zeta + \eta + \theta + = 1$）が主に形成される。

【0038】本発明に係る水素吸蔵合金（バナジウム基合金）には、添加した脱酸剤の一部が固溶している。特に、上記のようなV−Ti系固溶体合金では、母相及び第二相の少なくとも一方に脱酸剤（前記と同様のもの）が固溶した状態で存在している。本発明の製造方法において、合金原料に添加された脱酸剤は、通常は酸化物として合金系外に排出されるが、脱酸剤の一部は排出されずに合金中に固溶する。脱酸剤の固溶は、用いる脱酸剤の種類、合金組成等との組み合わせにもよるが、水素吸蔵特性のさらなる向上に寄与し得る。但し、固溶量が多すぎるとかえって特性を低下させることもあるので、通常は合金中2at.%以下、好ましくは1at.%以下とすれば良い。なお、下限値は、通常は0.5at.%程度とすれば良い。

【0039】本発明に係る水素吸蔵合金は、特にニッケル−水素化物電池等のアルカリ二次電池の水素化物電極（電池活物質）として有用である。この水素吸蔵合金の粉末を用い、公知の水素化物電極と同様の方法によって電極を作製することができる。例えば、合金粉末を必要に応じて公知の導電材（ニッケル粉等）等と混合し、集電体（ニッケルエキスパンドメタル等）とともにプレス成形等によりシート状に一体成形すれば良い。

【0040】
【発明の効果】本発明の製造方法によれば、以下のような効果が得られる。

【0041】（1）脱酸剤によってバナジウム中の酸素の少なくとも一部を酸化物として合金の組織外に排出することができるので、バナジウム系合金中の酸素含有量の低減を図ることができる。

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【0042】その結果、本発明の製造方法により得られる水素吸蔵合金の水素吸蔵量の大幅な増大を図ることができる。また、粒界における酸化物の偏析を抑制ないしは防止できることから、良好な三次元網目骨格を有する水素吸蔵合金が製造でき、この合金を電極として用いる場合には、優れた電極特性を得ることができる。特に、充放電の繰り返し等にも十分耐え得る優れた耐久性を発揮することができ、電池の放電容量の増大も図ることができる。

【0043】（2）本発明の製造方法では、高酸素濃度のバナジウム系合金原料を使用することができる。すなわち、テルミット還元によって得られる安価なバナジウム又はその合金もそのまま使用できるので、大幅な低コスト化を図ることができる。また、高酸素濃度のバナジウム系合金原料を使用できることから、かえって粉砕等は容易となり、秤量等も比較的簡単に行うことができ、その取扱い性等にも優れる。

【0044】（3）上記（2）のような安価なバナジウム系合金原料が使用できることから、本発明の製造方法は、効率面及びコスト面において非常に有利であり、工業的規模での生産にも適している。

【0045】
【実施例】以下、実施例を示し、本発明の特徴とするところをより一層明確にする。

【0046】実施例1
合金組成$V_{46} Ti_{40} Ni_{14}$のバナジウム基合金を各種の脱酸剤を用いて作製した。

【0047】バナジウム（V）としては、精製した酸化バナジウム粉末から、アルミニウム粉末を用いるテルミット還元により得た酸素含有量6000ppmのものを用いた。脱酸剤は、Ca、Mg、CaNi$_5$、Mg$_2$Ni又はLaの5種類をそれぞれ使用した。なお、CaNi$_5$とMg$_2$Niは、それぞれの合金100%のものではなかったが、平均組成はこの化学量論比に合致していた。

【0048】合金原料としてV、Ti及びNiの各破片をそれぞれ秤量した。但し、脱酸剤としてNiを含むCaNi$_5$とMg$_2$Niを用いる場合は、これら合金中のNi成分と、単金属として秤量したV、Ti及びNiを合わせて所定の合金組成となるように秤量した。

【0049】秤量は次のようにして行った。酸素含有量6000ppmのバナジウムは組成式$V_{0.981} O_{0.019}$と表わされる。従って、このバナジウムを用いた合金組成は、$V_{46} Ti_{40} O_{0.891}$となる。また、これまでの実験で鋳造後の酸素濃度が増加することが判明しており、また脱酸剤のすべてが還元には寄与しないと考えられることから、バナジウム中の酸素含有量の還元当量の2倍程度の脱酸剤を添加した。従って、例えば、脱酸剤としてCaNi$_5$を用いた場合は、

$(V_{0.981} O_{0.019})_{46.89} Ti_{40} Ni_{(14-8.74)} (CaNi_5)_{1.748}$

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となるように$V_{0.981}O_{0.019}$、Ti、Ni及びCaNi
$_5$をそれぞれ秤量した。

【0050】上記6000ppmの酸素を含むバナジウ
ムは、精製した酸化バナジウム粉末をテルミット還元し
て得たものであって、高真空雰囲気で行う電子ビーム精
製を行わないので低コストで済んだ。また、このバナジ
ウムは、固溶酸素のために容易に粉砕できるので合金の
秤量等の取扱いも容易であった。

【0051】次いで、合金原料を加熱溶解した後、所定
の脱酸剤を加え、再溶解を行った。溶解装置は、減圧ア
ルゴンアーク炉を用いた。アーク溶解の初期は、出力5
0W以下で行い、高融点金属の溶解と全体の混合を主目
的として行った。

【0052】続いて、溶湯をいったん冷却し、得られた
合金塊を反転し、再度溶解するという工程を数回繰り返
した。この溶解は200～500Wの出力で行った。こ
の過程で合金中の酸素が脱酸剤によって還元され、生成
した酸化物が合金組織（合金相）から排出されるととも
に、合金組成が均質化された。

【0053】この場合、単体であるCa又はMgを脱酸
剤として用いた場合には溶解中の酸化・還元反応が激し
くなるのに対し、La単体あるいはCaNi$_5$等の合金
を用いた場合には反応が比較的穏やかであるために反応
を制御しやすく、容易に溶解することができた。

【0054】なお、比較試料として、脱酸剤を使用しな
い以外は、上記と同様にして同じ合金組成のものを作製
した。さらに、参考試料として、脱酸剤を使用せず、か*

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*つ超高純度（酸素量350ppm）のバナジウムを用い
た以外は上記と同様にして同じ合金組成のものを作製し
た。

【0055】得られた鋳造合金についてその組織等を分
析した。本発明の鋳造合金の表面には、蛍光X線分析に
よって数％のCa、Mg又はLaが検出された。また、
本発明の鋳造合金の断面をSEM-EPMA（SEM：
走査型電子顕微鏡、EPMA：電子プローブマイクロア
ナライザ）で分析すると、バナジウム固溶体の母相と、
その粒界にTiとNiを高濃度で含む相とが認められ
た。どちらの相中にもMg及びCaが0.5～1at.％
程度検出された。また、Laは、バナジウム固溶体の粒
界にLa-Ni相として少量析出しており、これは還元
反応に寄与しなかったLaがNiと合金化して残留した
ものと考えられる。

【0056】次いで、各合金を水素化粉砕し、粉末化し
た後、真空中500℃で脱水素化したものをX線回折分
析により解析した。その結果、体心立方構造を有するバ
ナジウム固溶体（bcc（体心立方構造））のピークと
Ti_2Ni基相のピークとが見られた。これらに関して
は、参考試料も同様の結果であった。一方、比較試料
は、粒界にTi_2Ni及びTi_4Ni_2Oの析出が認めら
れた。得られた合金の組織、合金内の酸素濃度及び最大
水素吸蔵量を表1に示す。

【0057】
【表1】

表1

実施例1

脱酸剤	母相以外の組織	合金内酸素濃度(ppm)	最大水素吸蔵量(H/M)
Ca	Ti_2Ni	1700	1.56
CaNi$_5$	Ti_2Ni	700	1.63
Mg	Ti_2Ni	1200	1.54
Mg$_2$Ni	Ti_2Ni	900	1.67
La	Ti_2Ni, LaNi$_5$	800	1.66

比較試料・参考試料

バナジウム内酸素濃度	母相以外の組織	合金内酸素濃度(ppm)	最大水素吸蔵量
6000ppm	Ti_2Ni, Ti_4Ni_2O	8000	1.12
350ppm	Ti_2Ni	500	1.67

【0058】表1の結果より、脱酸剤を使用しなかった
比較試料は、最大水素吸蔵量が1.12（H/M）と低※50

※いことがわかる。これに対し、本発明の合金では、60
00ppmもの酸素を含有するバナジウム系合金原料を

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用いたにもかかわらず、酸素含有量３５０ｐｐｍの超高純度バナジウム系合金原料を用いた参考試料と同程度の高い最大水素吸蔵量を発揮できることがわかる。

【００５９】実施例２
合金組成$V_3TiNi_{0.56}Nb_{0.047}Ta_{0.047}Co_{0.05}Mo_{0.2}$（M＝Ｃａ、Ｍｇ又はＬａ）となるように、合金原料としてのＶ、Ｔｉ、Ｎｉ、Ｎｂ、Ｔａ及びＣｏ、脱酸剤としてのＣａＮｉ₅、Ｍｇ₂Ｎｉ及びＬａをそれぞれ秤量し、全体で６０ｇとなるようにした。バナジウム系合金原料としては、酸素含有量が５０００ｐｐｍのバナジウムを用いた。このバナジウムは、精製した酸化バナジウム粉末から、アルミニウム粉末によるテルミット還元によって得たものである。

【００６０】まず、これら合金原料を減圧アルゴン雰囲気下でアーク溶解し、鋳造合金を作製した。アーク溶解の初期は出力５０Ｗ以下で行い、高融点合金の溶解と全体の混合を行った。これにＣａＮｉ₅、Ｍｇ₂Ｎｉ又はＬａを入れ、溶解した。その後、溶湯をいったん冷却し、得られた合金塊を反転した後、再び溶解するという工程を数回繰り返した。この溶解は出力２００～５００Ｗで行い、この過程で合金中の酸素がＣａ、Ｍｇ又はＬａと反応して酸化物を形成し、これらの酸化物が合金外に排出されるとともに、合金組成の均質化を行った。

【００６１】なお、比較試料として、脱酸剤を使用しない以外は、上記と同様にして同じ合金組成のものを作製した。さらに、参考試料として、脱酸剤を使用せず、かつ超高純度（酸素含有量３００ｐｐｍ）のバナジウムを用いた以外は上記と同様にして同じ合金組成のものを作製した。

【００６２】得られた鋳造合金についてその組織等を分＊30

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＊析した。蛍光Ｘ線分析により、本発明の鋳造合金の表面には数％のＣａ、Ｍｇ、Ｌａがそれぞれ検出された。この合金の断面をＳＥＭ－ＥＰＭＡで分析すると、バナジウム固溶体の母相とその粒界に析出したＴｉＮｉ基相とが見られた。また、いずれの相にもＭｇ及びＣａが０.５～１ａｔ.％程度検出された。Ｌａを添加した合金では、少量のＬａ－Ｎｉ相が断面より観察され、またＴｉＮｉ相中に約１ａｔ.％のＬａが検出された。

【００６３】次いで、この合金を水素化粉砕し、粉末化した後、真空中５００℃で脱水素化したものをＸ線回折分析で解析すると、バナジウムの固溶体（ｂｃｃ）のピークとＴｉＮｉ基相のピークとが認められた。これらに関しては、参考試料も同様の結果であった。一方、比較試料では、脱酸剤を用いなかったために組織上の違いが認められた。すなわち、母相はバナジウム固溶体であったが、粒界にＴｉＮｉ基相のほかTi_4Ni_2O相と母相よりＴｉ濃度が高いバナジウム固溶体相が確認された。

【００６４】各合金を水素化した後に機械粉砕したものに銅粉を混合し、これをプレス成型して水素吸蔵合金電極を作製した。この電極を負極とし、正極にはカルボニルニッケルを用い、電解液として６ＭのＫＯＨ水溶液を用いて水素吸蔵合金電極の放電容量を測定した。測定の放電電流密度を合金当たり５０Ａｋｇ⁻¹又は２００Ａｋｇ⁻¹とした。また、充放電を繰り返し行い、このサイクルに対する耐久性を調べた。その結果を表２に示す。なお、表２には、得られた合金の合金内酸素濃度も併せて示す。

【００６５】
【表２】

表２

実施例２

脱酸剤	Ｖ内酸素濃度(ppm)	合金内酸素濃度(ppm)	C_1(50Akg⁻¹)(Ahkg⁻¹)	C_1(200Akg⁻¹)(Ahkg⁻¹)	100 C_{100}/C_1 (%)
CaNi₅	5000	1200	360	210	86
Mg₂Ni	5000	1500	350	200	83
La	5000	800	360	220	84

参考資料・比較試料

脱酸剤	Ｖ内酸素濃度(ppm)	合金内酸素濃度(ppm)	C_1(50Akg⁻¹)(Ahkg⁻¹)	C_1(200Akg⁻¹)(Ahkg⁻¹)	100 C_{100}/C_1 (%)
なし	300	600	360	200	88
なし	5000	7000	210	130	87

【００６６】表２の結果より、比較試料では、酸素含有※50※量が高いため、水素吸蔵量の増大を図ることができず、

放電容量も低いことがわかる。これに対し、本発明の製造方法による水素吸蔵合金では、超高純度バナジウムを用いた参考試料と同程度の優れた放電容量及び耐久性を発揮できることがわかる。

【００６７】実施例３
実施例２と同様の合金$V_3TiNi_{0.56}Nb_{0.047}Ta_{0.047}Co_{0.05}$を実施例２と同様にして作製した。但し、合金原料として、合金$V_3TiNi_{0.56}Nb_{0.047}Ta_{0.047}Co_{0.05}$（合金原料Ａ）及び合金$V_3TiNb_{0.047}Ta_{0.047}Co_{0.05}$（合金原料Ｂ）を用いた。

【００６８】まずＶ、Ｔｉ、Ｎｉ、Ｎｂ、Ｔａ及びＣｏを秤量し、アーク法により加熱溶解し、合金原料Ａ及び合金原料Ｂを作製した。この場合、バナジウムとしては酸素含有量３０００ｐｐｍのものを使用した。合金原料全体の酸素濃度（中間合金内酸素濃度）は５０００～６０００ｐｐｍであった。

【００６９】次いで、合金原料Ａには脱酸剤としてＭｇ、Ｃａ又はＭｍ（Ｍｍ：希土類元素の混合物）を使用し、合金原料Ｂには脱酸剤としてＣａＮｉ₅、Ｍｇ₂Ｎｉ又はＭｍＮｉ₅を加えて、それぞれ$V_3TiNb_{0.047}Ta_{0.047}Co_{0.05}(CaNi_5)_{0.114}$、$V_3TiNb_{0.047}Ta_{0.047}Co_{0.05}(Mg_2Ni)_{0.57}$、$V_3TiNb_{0.047}Ta_{0.047}(MmNi_5)_{0.114}$となるように調合した。水冷銅鋳型の底に脱酸剤Ｍｇ、Ｃａ、Ｍｍ、ＣａＮｉ₅、Ｍｇ₂Ｎｉ又はＭｍＮｉ₅を入れ、その上から予め溶解して合金化した粗合金を加え、アーク溶解することにより６種類の合金$V_3TiNi_{0.56}Nb_{0.047}Ta_{0.047}Co_{0.05}$を作製した。アーク溶解の初期は出力５０Ｗ以下で行うことにより合金と脱酸剤とを混合した。

【００７０】次に、合金を反転し、再溶解した。再溶解は２００～５００Ｗの出力で行い、この過程で合金中の酸素はＣａ、Ｍｇ又はＭｍと反応して、酸化物を合金系＊

＊外に排出すると同時に合金組織の均一化を図った。

【００７１】合金の作製時にＣａ、Ｍｇ、Ｍｍ、ＣａＮｉ₅、Ｍｇ₂Ｎｉ又はＭｍＮｉ₅を添加して溶製した場合には、次のような鋳造合金が得られた。すなわち、鋳造直後の鋳造合金表面には蛍光Ｘ線分析により数％のＣａ、Ｍｇ又はＭｍがそれぞれ検出された。また、この合金の断面をＳＥＭ－ＥＰＭＡで分析するとバナジウム固溶体の母相において、その粒界に析出したＴｉＮｉ相が認められた。また、いずれの相にもＭｇ、Ｃａ、Ｍｍが０．５～１ａｔ．％程度検出された。

【００７２】各合金を水素化粉砕し、粉末状にした後、５００℃の真空中で脱水素化したものをＸ線回折分析するとバナジウム固溶体（ｂｃｃ）のピークとＴｉＮｉ基相のピークが見られた。この点においては、実施例２の参考例の組織と同様であった。一方、高酸素濃度のバナジウムを用い、脱酸剤を添加しなかった合金では組織上の差異が認められた。すなわち、母相はバナジウム固溶体であったが、粒界にはＴｉＮｉ基相のほかにTi_4Ni_2O相と母相よりＴｉ濃度が高いバナジウム固溶体相が見られた。

【００７３】６種類の各合金を水素化後に機械粉砕したものに銅粉を混合し、これをプレス成形して水素吸蔵合金電極を作製した。この電極をカルボニルニッケル、電解液に６ＭのＫＯＨ水溶液を用いて水素吸蔵合金電極の放電容量を測定した。測定の放電電流密度を合金当たり$50Akg^{-1}$又は$200Akg^{-1}$とした。また、充放電を繰り返し行い、このサイクルに対する耐久性を調べた。これらの結果を中間合金内酸素濃度及び合金内酸素濃度とともに表３に示す。

【００７４】
【表３】

表3

実施例3

脱酸剤	中間合金内酸素濃度(ppm)	合金内酸素濃度(ppm)	$C_1(50Akg^{-1})$ (Ahkg⁻¹)	$C_1(200Akg^{-1})$ (Ahkg⁻¹)	$100\,C_{100}/C_1$ (%)
Ca	5000	1000	320	170	88
Mg	5000	1200	300	170	84
Mm	5000	900	380	180	83
CaNi₅	6000	800	380	200	84
Mg₂Ni	5000	600	390	210	78
MmNi₅	5000	900	370	200	82

【００７５】表３の結果より、本発明の製造方法による水素吸蔵合金は、高酸素濃度のバナジウム系合金原料を用いたにもかかわらず、実施例２参考試料と同程度の優れた電極特性を発揮していることがわかる。

【００７６】実施例４
$V_3TiNi_{0.56}Hf_{0.24}$は、第２相としてＴｉ－Ｎｉ－Ｖ系ＡＢ₂型ラーベス相が主となる三次元網目骨格を※

※有する合金である。合金$V_3TiNi_{0.56}Hf_{0.24}M_{0.2}$（Ｍ＝Ｃａ、Ｍｇ、Ｍｍ）の組成になるようにＶ、Ｔｉ、Ｎｉ、Ｈｆ及びＣａＮｉ₅、Ｍｇ₂Ｎｉ又はＭｍＮｉ₅を秤量し、全体で６０ｇにしたものを準備した。バナジウムとしては、酸素含有量が５０００ｐｐｍのものを用いた。このバナジウムは、精製した酸化バナジウム粉末をテルミット還元して得た通常の合金である。すなわ

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ち、高真空雰囲気下で電子ビーム精製を行った超高純度品ではないので、低コストで済んだ。しかも、固溶酸素のために容易に粉砕できるので合金の秤量等の取り扱いも容易であった。

【００７７】次いで、これら合金原料の溶解を行い、合金化した。水冷銅鋳型の底にまずＣａＮｉ₅、Ｍｇ₂Ｎｉ又はＭｍＮｉ₅を入れ、その上に溶解した粗合金を入れた。

【００７８】これを減圧下アルゴン雰囲気下でアーク溶解し、鋳造合金を作製した。アーク溶解の出力は初期では５０Ｗ以下とし、高融点金属の溶解と全体の混合を行った。次いで、溶湯をいったん冷却した後、得られた合金塊を反転し、冷却してから再び溶解する工程を数回繰り返した。この溶解は２００～５００Ｗの出力で行い、この過程で合金中の酸素はＣａ、Ｍｇ又はＭｍと反応して酸化物として合金系外に排出されると同時に、合金組成が均質化された。

【００７９】なお、比較試料として、脱酸剤を使用しない以外は、上記と同様にして同じ合金組成のものを作製した。さらに、参考試料として、脱酸剤を使用せず、かつ超高純度（酸素量３５０ｐｐｍ）のバナジウムを用いた以外は上記と同様にして同じ合金組成のものを作製した。

【００８０】得られた鋳造合金についてその組織等を分析した。蛍光Ｘ線分析により、本発明の鋳造合金の表面には数％のＣａ、Ｍｇ、Ｍｍがそれぞれ検出された。ま*

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*た、この合金の断面をＳＥＭ－ＥＰＭＡで分析すると、バナジウム固溶体の母相とその粒界に析出したＴｉ－Ｎｉ－Ｖ基ラーベス相が見られた。また、どちらの相にもＭｇ及びＣａが０．５～１ａｔ．％程度検出された。Ｍｍについては、母相中には検出されず、ラーベス相中に約１ａｔ．％検出された。

【００８１】各合金を水素化粉砕し、粉末状にした後、真空中５００℃で脱水素化したものをＸ線回折分析で解析するとバナジウムの固溶体（ｂｃｃ）のピークとラーベス相のピーク、さらに弱い強度でＴｉ₂Ｎｉ基相のピークが認められた。これらに関しては、参考試料の場合も同様であった。一方、比較試料では、脱酸剤を用いなかったので組織上の違いが見られた。すなわち、母相はバナジウムの固溶体であったが、粒界にはＴｉＮｉ基相のほかに、ＨｆＯ₂相とＴｉ₄Ｎｉ₂Ｏ相が認められた。

【００８２】各合金を水素化した後に機械粉砕し、次いで銅粉を混合し、この混合粉末をプレス成型して水素吸蔵合金電極を作製した。この電極を負極とし、正極としてカルボニルニッケルを用い、電解液に６ＭのＫＯＨ水溶液を用いて水素吸蔵合金電極の放電容量を測定した。測定の放電電流密度を合金当たり５０Ａｋｇ⁻¹又は２００Ａｋｇ⁻¹とした。また、充放電を繰り返し行い、このサイクルに対する耐久性を調べた。その結果を表４に示す。

【００８３】
【表４】

表４

実施例４

脱酸剤	Ｖ内酸素濃度(ppm)	合金内酸素濃度(ppm)	C_1(50Akg⁻¹)(Ahkg⁻¹)	C_3(200Akg⁻¹)(Ahkg⁻¹)	100 C_{100}/C_1(%)
CaNi₅	5000	1300	330	260	70
Mg₂Ni	5000	1000	330	240	64
MmNi₅	5000	900	340	240	74

参考資料・比較試料

脱酸剤	Ｖ内酸素濃度(ppm)	合金内酸素濃度(ppm)	C_1(50Akg⁻¹)(Ahkg⁻¹)	C_3(200Akg⁻¹)(Ahkg⁻¹)	100 C_{100}/C_1(%)
なし	350	290	350	290	72
なし	5000	7000	135	40	92

【００８４】表４の結果より、比較試料では、酸素含有量が高いため、水素吸蔵量の向上ができず、放電容量も低いことがわかる。これに対し、本発明品では、超高純度バナジウムを用いた参考試料と同程度の優れた放電容量及び耐久性を発揮できることがわかる。

【００８５】実施例５
合金Ｖ₄ＴｉＮｉ₀.₆₅Ｃｏ₀.₀₅Ｎｂ₀.₀₄₇Ｔａ₀.₀₄₇を作 ※50

※製した。

【００８６】合金原料Ｖ、Ｔｉ、Ｎｉ、Ｎｂ、Ｔａ及びＣｏ、さらに脱酸剤としてＣａＮｉ₅又はＭｇ₂Ｎｉをそれぞれ秤量し、Ｖ₄ＴｉＮｉ₀.₆₅Ｃｏ₀.₀₅Ｎｂ₀.₀₄₇Ｔａ₀.₀₄₇Ｍ₀.₀₂₉（Ｍ＝Ｃａ，Ｍｇ）となるようにした。バナジウムとしては、酸素含有量が２００ｐｐｍ以下の超高純度品を用いた。

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【００８７】水冷銅鋳型内にまず脱酸剤のＣａＮｉ₅又はＭｇ₂Ｎｉを入れ、その上に融点の低い順に合金原料を入れ、アルゴン雰囲気下でアーク溶解した。なお、比較試料として、ＣａＮｉ₅及びＭｇ₂Ｎｉを添加しない以外は、上記の同様にして同じ組成のものを作製した。

【００８８】本発明の鋳造合金の断面をＳＥＭ－ＥＰＭＡで分析すると、バナジウム固溶体の母相とその粒界に析出したＴｉＮｉ相が見られた。また、バナジウム固溶体相にはＭｇ、Ｃａが約０．５ａｔ．％検出された。この合金を高温の水素雰囲気下で水素化させ、そのまま室温に冷却することで鋳造合金塊を水素化粉砕した。

【００８９】どの合金についても、結晶構造はバナジウム固溶体とＴｉＮｉ基相による２つのｂｃｃ構造をもつことが確認された。母相の格子定数はほとんど変化していなかった。また、微細構造にも変化が見られなかった。なお、合金中の酸素含有量は、比較試料が６００ｐｐｍ、ＣａＮｉ₅及びＭｇ₂Ｎｉを添加したものはそれぞれ５００ｐｐｍ及び４００ｐｐｍであった。

【００９０】各合金についての平衡圧－組成等温曲線（ＰＣＴ曲線）を図１に示す。各合金の２９３Ｋの３．３－０．０１ＭＰａでの放出水素量（Ｈ／Ｍ）は、比較試料では０．６３、ＣａＮｉ₅を添加した合金は０．６６、Ｍｇ₂Ｎｉ添加合金では０．６４であり、最も高い値となった。これは、Ｃａが母相へ固溶したことによるほか、溶製時に合金内の固溶酸素がＣａによって還元されたことによるものと考えられる。このようなＰＣＴ曲線から、放電容量は大きな値になることが予想される。

【００９１】各合金を粒径７５μｍ以下に機械粉砕したものを３倍の質量の銅粉末と混合した後、成型圧７．５ｔ／ｃｍ²で錠剤成型したものを電極とした。この電極の活性化特性として、放電電流密度ｉ₍ｄ₎＝２５Ａｋｇ⁻¹（ｍＡｇ⁻¹）で１０サイクルの充放電サイクル中の放電容量の変化を調べた（図２）。その後、ｉ₍ｄ₎＝４０～４００Ａｋｇ⁻¹で高率放電特性を調べ（図３）、引き続き

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ｉ₍ｄ₎＝２５Ａｋｇ⁻¹で充放電サイクル試験を行い、耐久性について調べた（図４）。なお、参照極はＨｇ－ＨｇＯ、充電は１００Ａｋｇ⁻¹で５ｈ、カットオフ電位は－０．７５Ｖ ｖｓ．Ｈｇ－ＨｇＯで測定温度は２９３Ｋとした。

【００９２】活性化特性は、図２に示すように１サイクル目で最高放電容量の７６％以上の容量になり、どの合金も優れた立ち上がりを見せた。ＣａＮｉ₅を添加した合金では比較試料に比して約１０％高い３６１Ａｋｇ⁻¹の放電容量となった。Ｍｇ₂Ｎｉを添加したものも性能の向上が見られた。

【００９３】高率放電特では、図３に示すようにＣａＮｉ₅、Ｍｇ₂Ｎｉの添加によりｉ₍ｄ₎≦２００Ａｋｇ⁻¹で放電容量が向上した。ＣａＮｉ₅を添加した場合は、ｉ₍ｄ₎＝２００Ａｋｇ⁻¹で２２０Ａｋｇ⁻¹の放電容量が得られた。Ｍｇ₂Ｎｉ添加の場合も同様の性能向上が認められた。

【００９４】また、充放電サイクル特性についても、図４に示すようにいずれの合金も良好であった。

【００９５】図１～図４に示すように、本発明の製造方法では、安価な高酸素量のバナジウム系原料を有効に使用できることはもとより、超高純度（低酸素量）のバナジウム系合金原料を用いた場合はより優れた特性が得られることがわかる。
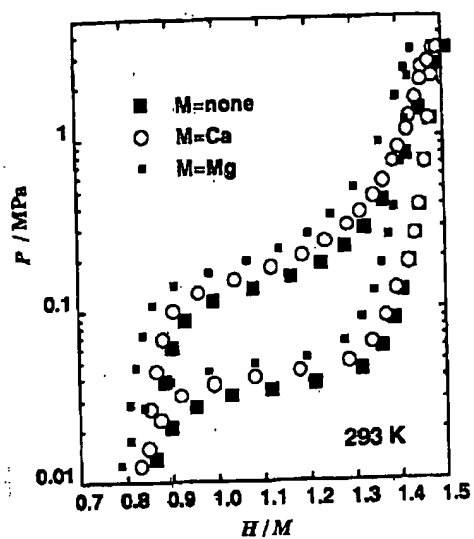
【図面の簡単な説明】

【図１】実施例５で作製した各合金における平衡圧－組成等温曲線である。

【図２】実施例５で作製した各合金からなる電極における活性化特性を示す図である。
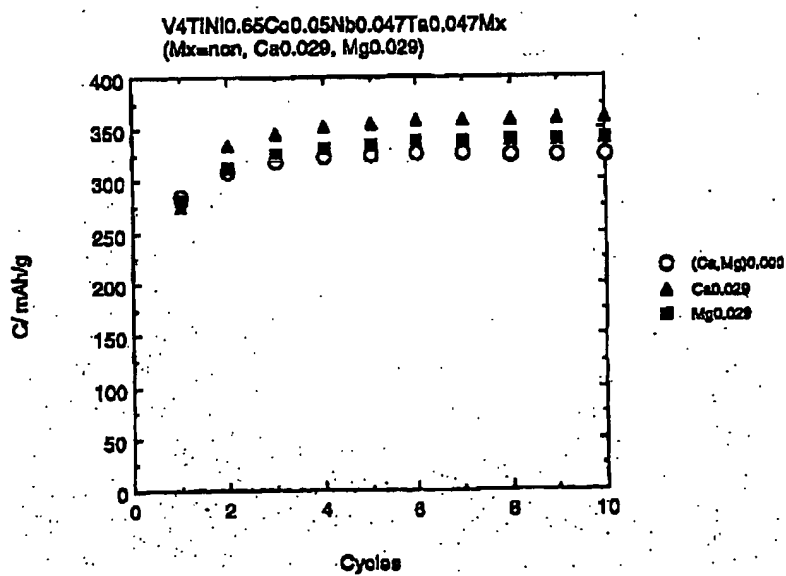
【図３】実施例５で作製した各合金からなる電極における高率放電特性を示す図である。

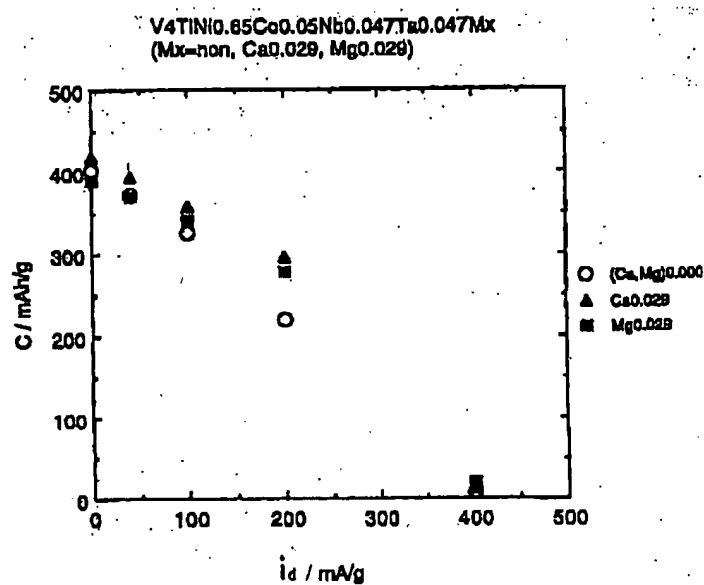【図４】実施例５で作製した各合金からなる電極における充放電サイクル特性を示す図である。

【図1】

V₄TINI₀.₆₅Co₀.₀₅Nb₀.₀₄₇Ta₀.₀₄₇M₀.₀₂₉
の組成−圧力−等温線

$V_4TINI_{0.65}Co_{0.05}Nb_{0.047}Ta_{0.047}M_{0.029}$ の組成−圧力−等温線

【図2】

V4TINI0.65Co0.05Nb0.047Ta0.047Mx
(Mx=non, Ca0.029, Mg0.029)

【図3】

V4TiNi0.65Co0.05Nb0.047Ta0.047Mx
(Mx=non, Ca0.029, Mg0.029)

【図4】

V4TiNi0.65Co0.05Nb0.047Ta0.047Mx
(Mx=non, Ca0.029, Mg0.029)
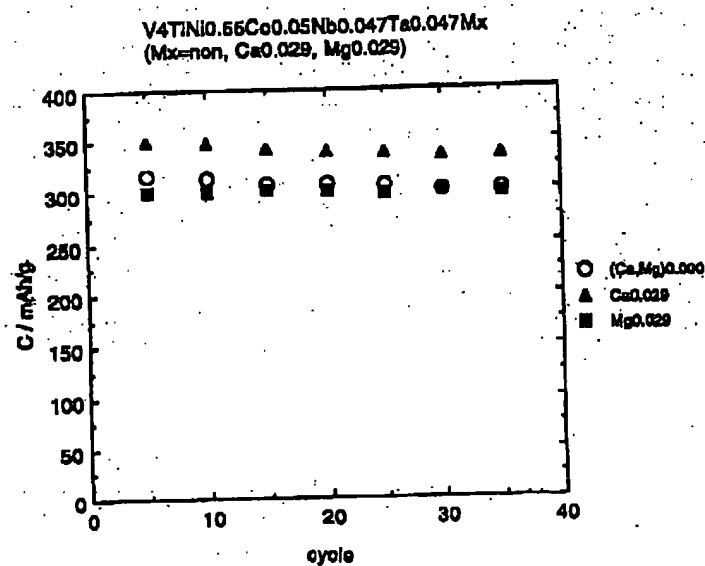

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture method of the hydrogen storing metal alloy which is the manufacture method of the hydrogen storing metal alloy which consists of a vanadium machine alloy, and is characterized by carrying out the heating dissolution of the vanadium system alloy raw material with at least one sort of a deoxidizer.

[Claim 2] The manufacture method according to claim 1 that the oxygen content of a vanadium system alloy raw material is 2000-20000 ppm.

[Claim 3] The manufacture method according to claim 1 from which some or all of a vanadium system alloy raw material is obtained by a thermite reduction method.

[Claim 4] The manufacture method according to claim 1 which is what a deoxidizer reacts selectively with the oxygen contained in a vanadium system alloy raw material, and is discharged out of an alloy system as an oxide.

[Claim 5] The manufacture method of Ca, Mg, rare earth elements, and these alloys according to claim 4 that the number of deoxidizers is one at least.

[Claim 6] The manufacture method of Ca, Mg, and rare earth elements according to claim 5 that a deoxidizer is the alloy of one sort and nickel at least.

[Claim 7] The manufacture method according to claim 6 that a deoxidizer is at least one sort of a Ca-nickel system alloy.

[Claim 8] The manufacture method according to claim 6 that a deoxidizer is at least one sort of a Mg-nickel system alloy.

[Claim 9] The manufacture method according to claim 6 that a deoxidizer is at least one sort of a rare-earth-elements-nickel system alloy.

[Claim 10] The hydrogen storing metal alloy which is a vanadium machine alloy obtained by the method according to claim 1 to 9, and is characterized by a part of added deoxidizer [at least] dissolving in the alloy concerned.

[Claim 11] The hydrogen storing metal alloy according to claim 10 whose amount of dissolution of a deoxidizer is 0.5-2at.%.

[Claim 12] The hydrogen storing metal alloy according to claim 10 or 11 characterized by for the second phase which uses a TiNi phase as a principal component forming a three-dimensions network frame, and existing in the host phase which is a vanadium machine alloy and consists of a V-Ti system solid solution alloy, and the

deoxidizer dissolving to either [at least] a host phase or the second phase.

[Claim 13] In the host phase which is a vanadium machine alloy and consists of a V-Ti system solid solution alloy, the second phase which makes the main phase the Ti-nickel-V system AB2 type Laves phase forms a three-dimensions network frame, and exists. And the hydrogen storing metal alloy according to claim 10 or 11 characterized by the deoxidizer dissolving to either [at least] a host phase or the second phase.

[Claim 14] The hydride electrode using a hydrogen storing metal alloy according to claim 10 to 13.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture method of the hydrogen storing metal alloy which consists of a vanadium machine alloy. Furthermore, it is related with the hydride electrode using the hydrogen storing metal alloy obtained by the manufacture method, and its alloy.

[0002]

[Description of the Prior Art] As a hydrogen storing metal alloy in the former The alloy with which the second phase which makes the main phase the second phase or the **Ti-nickel-V system AB2 type Laves phase which uses **TiNi phase as a principal component as the second phase forms the three-dimensions network frame into the host phase which consists of a V-Ti system solid solution alloy is known (JP,H7-268513,A, JP,H7-268514,A).

[0003] When using these alloys as negative electrode active material of an alkali secondary battery, the following effects are acquired by existence of the three-dimensions network frame which is the second phase. That is, since the second phase exists in the state of wrapping in a host phase, it can control the pulverization accompanying hydrogen absorption substantially. Moreover, the second phase serves as an overcoat to a host phase, and the dissolution of vanadium which is the principal component of a hydrogen storing metal alloy can be controlled or prevented. And improvement of endurance to a repetition of charge and discharge, neglect, etc. can be aimed at by these.

[0004] Furthermore, since the second phase functions as a reaction catalyst or an electronic conductor (collector) which a hydrogen storing metal alloy exchanges at hydrogenation and the dehydrogenation reaction of an alloy, it can increase the rate of reaction at the time of discharge.

[0005] And these hydrogen storing metal alloys are manufactured by carrying out the heating dissolution of these and carrying out cooling coagulation by the well-known dissolution methods, such as an arc melting method and induction heating, after usually carrying out the weighing capacity of the raw material metal so that it may become a predetermined presentation.

[0006] by the way, in the hydrogen storing metal alloy which consists of a vanadium machine alloy when vanadium contains oxygen It is reported that a hydrogen storage capacity decreases remarkably (J. J.Rcilly and R.H.Wiswall Jr.; BNL-16546 (Brookhaven National Laboratory, Upton, N.Y., 1972)). For this reason, in a hydrogen storing metal alloy, it is necessary to stop as low as possible the amount of oxygen contained in a vanadium solid solution phase.

[0007] The Thermit process (thermite reduction method) is conventionally used for manufacture of the inexpensive vanadium system alloy for steel addition widely. This mixes reducing material metals, such as an

aluminium, with the powder of a banazin san ghost, heats a mixture in a fireproof crucible, advances a reduction reaction, and completes a reaction further using the self-heating of a reaction. As a reducing material metal, the aluminium is used well, for example and the reduction reaction in that case is as follows.

[0008] 3 -- both are separated by depositing on a bottom the metallic vanadium (only henceforth "vanadium") which surfaced in the upper part of the fireproof crucible since the oxide of these reducing material metals had small specific gravity after a V2O5+10aluminum->6V+5 Al2O3 reduction reaction, and it was returned and was generated.

[0009]

[Problem to be solved by the invention] [however, the vanadium obtained by this method] The oxide which it is not fully returned in many cases since reaction time is short, and was generated by the reduction reaction will remain easily also in vanadium, and, generally high-concentration oxygen of 10000-20000 ppm will usually exist in vanadium as the result. The hydrogen storing metal alloy obtained by carrying out the heating dissolution with other elements also contains oxygen of this level using this vanadium. And since the oxygen to contain occupies the hydrogen occupancy site in a hydrogen storing metal alloy, a big hydrogen storage capacity cannot be expected and function sufficient as a hydrogen storing metal alloy cannot be exhibited.

[0010] Therefore, especially this invention primarily aims to manufacture the hydrogen storing metal alloy which can demonstrate the outstanding electrode characteristic using the vanadium of high oxygen concentration obtained by low cost, or its alloy.

[0011]

[Means for solving problem] As a result of repeating investigation wholeheartedly in view of the problem of the above-mentioned conventional technique, this invention person finds out that the above-mentioned object can be attained, when manufacturing a hydrogen storing metal alloy by the specific manufacture method, and came to complete this invention at last.

[0012] That is, this invention is the manufacture method of the hydrogen storing metal alloy which consists of a vanadium machine alloy, and relates to the manufacture method of the hydrogen storing metal alloy characterized by carrying out the heating dissolution of the vanadium system alloy with at least one sort of a deoxidizer.

[0013] Moreover, this invention is the vanadium machine alloy obtained by the above-mentioned manufacture method. In the host phase which consists of a **V-Ti system solid solution alloy especially, the second phase which uses a TiNi phase as a principal component forms a three-dimensions network frame, and exists. And the hydrogen storing metal alloy characterized by the deoxidizer dissolving to either [at least] a host phase or the second phase, Or the hydrogen storing metal alloy characterized by for the second phase which makes the main phase the Ti-nickel-V system AB2 type Laves phase forming a three-dimensions network frame, and existing in the host phase which consists of a **V-Ti system solid solution alloy, and the deoxidizer dissolving to either [at least] a host phase or the second phase is started.

[0014] Furthermore, this invention relates also to the hydride electrode using the hydrogen storing metal alloy obtained by the above-mentioned manufacture method.

[0015]

[Mode for carrying out the invention] As a vanadium system alloy raw material used by this invention, especially as long as vanadium is included, it is not restricted. For example, the mixture of vanadium or a vanadium alloy, an other metals, an alloy, etc., etc. can be used. Moreover, the vanadium alloy of the

presentation as a desired hydrogen storing metal alloy with the same presentation of a metal component can also be used as this invention vanadium system alloy raw material as it is, for example.

[0016] As a mixture of vanadium or a vanadium alloy, an other metals, an alloy, etc., etc. What mixed metals, such as a titanium raw material, a nickel raw material, a tantalum raw material, a cobalt material, a hafnium raw material, and a zirconium raw material, an alloy, etc. to vanadium or a vanadium alloy according to desired alloy composition, an alloy organization, etc. can be used.

[0017] As a vanadium alloy, vanadium machine alloys, such as ferrovanadium and nickel vanadium, etc. are mentioned, for example. In addition, alloys containing vanadium, such as two element systems, three element systems, and plural systems, can also be used as they are. In addition, the "alloy" as used in the field of this invention is the concept containing not only an alloy but an intermetallic compound (also following the same).

[0018] By this invention, an oxygen content (henceforth "oxygen concentration") can also use effectively in particular the vanadium system alloy raw material of high oxygen concentration which is 2000 ppm or more. That is, although about 2000-20000 ppm oxygen usually contains in the vanadium system alloy raw material, the hydrogen storing metal alloy which was excellent in this invention also from such a vanadium system alloy raw material of high oxygen concentration can be manufactured. Since the vanadium system alloy raw material of high oxygen concentration can generally be obtained inexpensive and it is moreover easy to grind it, it is advantageous especially in respect of the handling at the time of carrying out weighing capacity being easy, and occurring etc. On the other hand, in this invention, if a vanadium system alloy raw material with low oxygen concentration is used, the hydrogen storing metal alloy which demonstrates the characteristics which were so much excellent will be obtained. In addition, the ppm unit in this invention shows "mass ppm" (also following the same).

[0019] By the manufacture method of this invention, the portion or the vanadium oxide which made all and was refined, for example of a vanadium system alloy raw material can be used as a starting material, and the vanadium obtained from this raw material by the thermite reduction method by metallic aluminum or its alloy can be used conveniently. Generally, since vanadium by a thermite reduction method or its alloy is contained after oxygen has dissolved, or it is contained as a compound like V16O3, it is easy to crush, and it is cheap and advantageous in respect of cost. Moreover, in a thermite reduction method, it is also possible to use the vanadium returned in inert gas or a vacuum using magnesium or calcium as a reducing material metal or its alloy.

[0020] Moreover, you may contain the oxygen contained in a vanadium system alloy raw material with what kind of form. For example, as mentioned above, you may dissolve and exist in vanadium or may exist as an oxide (for example, V16O3 grade).

[0021] As a deoxidizer in this invention, it reacts with a part of oxygen [at least] contained in a vanadium system alloy raw material, and it is not restricted as long as abatement of the oxygen content can be aimed at. What reacts selectively with the oxygen especially contained in a vanadium system alloy raw material, and can be discharged out of an alloy system as an oxide is desirable. What is necessary is just the deoxidizer that it specifically reacts selectively with the oxygen contained in a raw material, an oxide is generated, and this oxide is substantially discharged outside the organization of a hydrogen storing metal alloy.

[0022] In this invention, there are also few Ca, Mg, rare earth elements, and these alloys, one sort is desirable, and the alloy of Ca, Mg, and rare earth elements which consists of one sort and nickel at least is especially more desirable.

[0023] As such an alloy, for example A Ca-nickel system alloy (CaNi5, CaNi2 grade), a Ca-aluminum system alloy (CaAl2 grade) and a Mg-nickel system alloy (Mg -- 2 nickel) Rare earth elements, such as MgNi2 grade, a Mg-aluminum system alloy (Mg2aluminum3 grade), La, and Ce, or the alloy of the mixture (Mm: misch metal) and nickel ([LaNi and]) CeNi2, MmNi5 grades, these mixtures, or solid solutions (Ca-Mg-La-nickel system alloy etc.) are mentioned. It is desirable at the point of comparing when simple substances, such as Ca, Mg, La, and Ce, are used especially for a Ca-nickel system alloy, a Mg-nickel system alloy, a La(or Ce)-nickel system alloy, etc. also in these deoxidizers, and being easy to control the reaction under dissolution.

[0024] about 1 to 3 times of the reducing equivalent of the oxygen usually contained in a vanadium system alloy raw material although the addition of a deoxidizer can be suitably set up according to the class of deoxidizer to be used etc. -- desirable -- 1.2 - double precision -- then, it is good.

[0025] Subsequently, weighing capacity is carried out so that it may become the presentation of a request of these alloy raw material, and after carrying out the heating dissolution (it is also only called "the dissolution") and alloying these alloy raw material, it remelts by supplying a deoxidizer.

[0026] Especially if the method of dissolving is under inert gas (argon, helium, etc.) atmosphere or a vacuum, it will not be restricted, but it should just carry out the heating dissolution according to a well-known method. As for especially the dissolution, it is desirable to carry out agitating in order to abolish the temperature gradient of a molten metal. In such a point, well-known dissolution equipment, such as an arc melting furnace and a high-frequency-induction-heating fusion furnace, can be used conveniently. In addition, when dissolving at an arc melting furnace, in order to prevent volatilization of the deoxidizer in early stages of the dissolution, it is desirable to make it not expose a deoxidizer to a direct arc in the phase in early stages of the dissolution. When using a high-frequency-induction-heating fusion furnace, it is desirable to a molten metal powdered or to blend a deoxidizer as the shape of granulation (mean particle diameter of 100 micrometers - about 10mm).

[0027] Moreover, in the dissolution, once cooling a molten metal, for example, while attaining homogenization of the organization of the casting alloy obtained by repeating several times in the process of reversing an alloy lump and dissolving again, blowdown of an oxide etc. can be promoted out of an alloy organization.

[0028] At a dissolution process, each element changes to the liquid phase, and the oxygen contained in the vanadium system alloy raw material (especially vanadium) reacts with a deoxidizer, and is discharged out of an alloy system as an oxide. Moreover, an unreacted deoxidizer usually has few amounts of dissolution to an alloy as [below] 5at.%, and what cannot dissolve forms a phase in the state where it generally dissociated with the alloy.

[0029] The oxide which reacted with the deoxidizer and was generated in the alloy deposits, for example to a casting alloy lump's surface, a grain boundary (inside of the second phase), etc., or, specifically, remains as slag in a furnace. On the other hand, the deoxidizer which did not contribute to a reaction with oxygen will dissolve in an alloy, or the part beyond the dissolution range will form a phase in the state where it dissociated with the alloy.

[0030] Thus, since a deoxidizer is discharged as an oxide in a dissolution process at the outside of an alloy organization, most oxides do not remain in the hydrogen storing metal alloy obtained. In particular, an oxide does not exist in the host phase in a hydrogen storing metal alloy, but is substantially constituted only from a vanadium solid solution.

[0031] However, the deoxidizer, the oxide, etc. may remain in one part of the hydrogen storing metal alloys within limits which do not bar the effect of this invention (as long as the oxygen content of a host phase can be

reduced especially). For example, although a part of deoxidizer may remain in the state where it dissolved in the alloy (a host phase, a grain boundary, etc.), since it can contribute to the improvement in characteristics as a hydrogen storing metal alloy as long as the oxygen content in an alloy host phase can be reduced at least also in this case, it is included by this invention.

[0032] In this invention, cooling is performed, after carrying out the heating dissolution. Especially the cooling method can be cooled by the slow cooling coagulation by not being restricted, for example, neglecting it in a furnace and in the air, the rapid solidification slushed into a water cooler, the super-rapid solidification dropped at the rotating copper roll, etc. In this case, the crystal grain diameter of a host phase, the deposit form of the second phase, etc. are controllable by controlling a cooling rate.

[0033] Since-izing of the oxygen concentration can be effectively carried out [****] by the activity of a deoxidizer by the manufacture method of this invention, it is possible to be able to apply to manufacture of the hydrogen storing metal alloy which consists of a vanadium machine alloy of two element systems or plural systems, and to also make the second various phase form according to desired performance (cell) etc.

[0034] Therefore, in the manufacture method of this invention, the vanadium machine alloy with which a part of added deoxidizer [at least] dissolved can also be obtained. For example, the hydrogen storing metal alloy which consists of the following V-Ti system solid solution alloys can be manufactured.

[0035] (1) the hydrogen storing metal alloy which the second phase which uses a TiNi phase as a principal component forms a three-dimensions network frame, and exists in a V-Ti system solid solution alloy in the host phase which consists of a V-Ti system solid solution alloy -- for example, what is necessary is just to blend each raw material so that it may be set to alloy composition $V_{alpha}Ti_{Nibeta}M_{gamma}$ (however, M -- at least one sort of Cr, Mn, Fe, Co, Cu, Nb, and Ta, $1<=alpha<=10$, $0.2<=beta<=2$, and $0.02<=gamma<=0.5$) in this case, $TiNi_{delta}N_{epsilon}$ (however, N -- at least one sort of V, Cr, Mn, Fe, Co, Cu, Nb, and Ta, $0.5<=delta<=2$, and $0.1<=epsilon<=1$) is mainly formed as an alloy phase (the second phase) which uses a TiNi phase as a principal component.

[0036] (2) case [of the hydrogen storing metal alloy which the alloy phase which makes the main phase the Ti-nickel-V system AB2 type Laves phase forms a three-dimensions network frame, and exists in a V-Ti system solid solution alloy in the host phase which consists of a V-Ti system solid solution alloy] ** -- for example, what is necessary is just to blend so that it may be set to alloy composition $V_{alpha}Ti_{Nibeta}A_{gamma}M_{delta}$ (however, A -- at least one sort of Zr, Hf, and Ta, and M -- at least one sort of Cr, Mn, Fe, Co, Cu, and Nb, $1<=alpha<=10$, $0.2<=beta<=2$, $0.05<=gamma<=1$, and $0< delta<=2$) AB2 type Laves phase as an alloy phase (the second phase) made into the main phase In this case, $Ti_{epsilon}A_{zeta}nickel_{eta}V_{theta}M_{iota}$ however, A -- at least one sort of Zr, Hf, and Ta, and M -- Cr and Mn -- At least one sort of Fe, Co, Cu, and Nb, $0.1<=epsilon<=0.4$, $0.1<=zeta<=0.4$, $0.1<=eta<=0.6$, $0.1<=theta<=0.5$, $0< iota<=0.2$, and $epsilon+zeta+eta+theta+iota = 1$ is mainly formed.

[0037] ** for example, what is necessary is just to blend so that it may be set to alloy composition $V_{alpha}Ti_{Nibeta}A_{gamma}$ (however, A -- at least one sort of Zr, Hf, and Ta, $1<=alpha<=10$, $0.2<=beta<=2$, and $0.05<=gamma<=1$) AB2 type Laves phase as an alloy phase (the second phase) made into the main phase In this case, $Ti_{epsilon}A_{zeta}nickel_{eta}V_{theta}$ (-- however, A -- at least one sort of Zr, Hf, and Ta, and $0.1<=epsilon<= -- 0.4$, $0.1<=zeta<=0.4$, and $0.1<=eta<= -- 0.6$, $0.1<=theta<=0.5$, and $epsilon+zeta+eta+theta +=1$) are mainly formed.

[0038] A part of added deoxidizer is dissolving in the hydrogen storing metal alloy (vanadium machine alloy)

concerning this invention. In particular, with the above V-Ti system solid solution alloys, in either [at least] a host phase or the second phase, after the deoxidizer (the same thing as the above) has dissolved, it exists. In the manufacture method of this invention, although the deoxidizer added by the alloy raw material is usually discharged out of an alloy system as an oxide, a part of deoxidizer dissolves in an alloy, without being discharged. Although dissolution of a deoxidizer is based also on combination with the class of deoxidizer to be used, alloy composition, etc., it can contribute to the further improvement in hydrogen absorption characteristics. However, what is necessary is for below 1at.% just to usually make [below 2at/ in an alloy /.%] it desirable, since characteristics may be reduced on the contrary when there are too many amounts of dissolution. In addition, a lower limit should just usually be taken as a 0.5at.% grade.

[0039] Especially the hydrogen storing metal alloy concerning this invention is useful as a hydride electrode (battery active material) of alkali secondary batteries, such as a nickel hydride cell. An electrode is producible by the same method as a well-known hydride electrode using the powder of this hydrogen storing metal alloy. For example, what is necessary is to mix after alloy powder with well-known conducting materials (nickel powder etc.) etc. if needed, and just to carry out integral moulding to the shape of a sheet by press forming etc. with collectors (nickel expanded metal etc.).

[0040]

[Effect of the Invention] According to the manufacture method of this invention, the following effects are acquired.

[0041] (1) Since it can discharge outside the organization of an alloy by a deoxidizer by using a part of oxygen [at least] in vanadium as an oxide, abatement of the oxygen content in a vanadium system alloy can be aimed at.

[0042] As a result, large buildup of the hydrogen storage capacity of the hydrogen storing metal alloy obtained by the manufacture method of this invention can be aimed at. Moreover, when the hydrogen storing metal alloy which has a good three-dimensions network frame can be manufactured and it uses this alloy as an electrode from the ability of the segregation of the oxide in a grain boundary to be controlled or prevented, the outstanding electrode characteristic can be acquired. The outstanding endurance which can be equal to a repetition of charge and discharge etc. enough especially can be demonstrated, and buildup of the service capacity of a cell can also be aimed at.

[0043] (2) By the manufacture method of this invention, the vanadium system alloy raw material of high oxygen concentration can be used. That is, since the inexpensive vanadium obtained by thermite reduction or its alloy can also be used as it is, large low cost-ization can be attained. Moreover, from the ability of the vanadium system alloy raw material of high oxygen concentration to be used, on the contrary, grinding etc. becomes easy, can perform weighing capacity etc. comparatively easily, and is excellent in the handling nature etc.

[0044] (3) Since an inexpensive vanadium system alloy raw material like the above (2) can be used, the manufacture method of this invention is dramatically advantageous in an efficiency side and a cost side, and suitable also for output on industrial magnitude.

[0045]

[Working example] Hereafter, an example is shown and the place by which it is characterized [of this invention] is clarified further.

[0046] The vanadium machine alloy of example 1 alloy-composition V46Ti40nickel14 was produced using various kinds of deoxidizers.

[0047] As vanadium (V), the thing with an oxygen content of 6000 ppm obtained by the thermite reduction using the end of aluminium powder was used from the refined vanadium oxide powder. Five kinds, Ca, Mg, CaNi5, Mg2nickel, or La, were used for the deoxidizer, respectively. In addition, although CaNi5 and Mg2nickel were not the things of 100% of each alloy, average composition had agreed in this stoichiometric mixture ratio.

[0048] The weighing capacity of each fragment of V, Ti, and nickel was carried out as an alloy raw material, respectively. However, when CaNi5 and Mg2nickel which contain nickel as a deoxidizer were used, weighing capacity was carried out so that V, Ti, and nickel which carried out weighing capacity as nickel component and the single metal in these alloys might be set and it might become predetermined alloy composition.

[0049] Weighing capacity was performed as follows. Vanadium with an oxygen content of 6000 ppm is expressed as empirical formula $V_{0.981}O_{0.019}$. Therefore, the alloy composition using this vanadium serves as $V_{46}Ti_{40}O_{0.891}$. Moreover, it had become clear that the oxygen concentration after casting increased in an old experiment, and since it was thought that not all the deoxidizers contributed to reduction, the deoxidizer about the double precision of the reducing equivalent of the oxygen content in vanadium was added. When it followed, for example, CaNi5 was used as a deoxidizer, the weighing capacity of $V_{0.981}O_{0.019}$, Ti, and nickel and CaNi5 was carried out, respectively so that it might be set to $46.89(V_{0.981}O_{0.019})$ Ti_{40}nickel $(14-8.74)$ $(CaNi5)_{1.748}$.

[0050] Vanadium containing 6000 above-mentioned ppm oxygen obtained it by having carried out thermite reduction of the refined vanadium oxide powder, and since it did not perform electron beam refining performed in high vacuum atmosphere, it was able to be managed with low cost. Moreover, since this vanadium was ground easily because of dissolution oxygen, handling of the weighing capacity of an alloy etc. was also easy for it.

[0051] Subsequently, after carrying out the heating dissolution of the alloy raw material, it remelted by adding a predetermined deoxidizer. The reduced pressure argon electric arc furnace was used for dissolution equipment. It carried out by less than output 50W, and the dissolution of a refractory metal and the whole mixing were performed as a key objective the early stages of arc melting.

[0052] Then, the molten metal was once cooled, the obtained alloy lump was reversed, and the process of dissolving again was repeated several times. This dissolution was performed with the output of 200-500W. Oxygen in an alloy was returned by the deoxidizer in this process, and alloy composition was uniformed while the generated oxide was discharged from the alloy organization (alloy phase).

[0053] In this case, to the oxidation-reduction reaction under dissolution becoming intense when Ca or Mg which is a simple substance is used as a deoxidizer, since the reaction was comparatively moderate when the alloy of La simple substance or CaNi5 grade is used, it was easy to control a reaction, and it was able to dissolve easily.

[0054] In addition, the thing of the same alloy composition was produced like the above as a comparison sample except not using a deoxidizer. Furthermore, the thing of the same alloy composition was produced like the above except not having used a deoxidizer and having used vanadium of super high purity (the amount of oxygen of 350 ppm) as a reference sample.

[0055] The organization etc. was analyzed about the obtained casting alloy. In the surface of the casting alloy of this invention, Ca of several percent, Mg, or La was detected by X-ray fluorescence. Moreover, when the cross section of the casting alloy of this invention was analyzed by SEM-EPMA (SEM: a scanning electron microscope, EPMA:electron probe microanalyzer), the host phase of a vanadium solid solution and the phase

which contains Ti and nickel by high concentration in the grain boundary were accepted. 0.5-1at.% grade detection of Mg and Ca was carried out also into which phase. Moreover, La has deposited in small quantities as a La-nickel phase to the grain boundary of a vanadium solid solution, and it is thought that La which did not contribute to a reduction reaction alloyed this with nickel, and it remained.

[0056] Subsequently, after carrying out hydrogenation grinding and carrying out disintegration of each alloy, what carried out dehydrogenation at 500 degrees C among the vacuum was analyzed by X-ray diffraction analysis. As a result, the peak of a vanadium solid solution (bcc (body-centered cubic structure)) and the peak of a Ti2nickel machine phase which have body-centered cubic structure were seen. It was a result also with reference sample same about these. On the other hand, as for the comparison sample, the deposit of Ti2nickel and Ti4nickel 2O was accepted in the grain boundary. The oxygen concentration and the maximum hydrogen storage capacity in the organization of the obtained alloy and an alloy are shown in Table 1.

[0057]

[Table 1]
表 1

実施例 1

脱酸剤	母相以外の組織	合金内酸素濃度(ppm)	最大水素吸蔵量(H/M)
Ca	Ti$_2$Ni	1700	1.56
CaNi$_5$	Ti$_2$Ni	700	1.63
Mg	Ti$_2$Ni	1200	1.54
Mg$_2$Ni	Ti$_2$Ni	900	1.67
La	Ti$_2$Ni, LaNi$_5$	800	1.66

比較試料・参考試料

バナジウム内酸素濃度	母相以外の組織	合金内酸素濃度(ppm)	最大水素吸蔵量
6000 ppm	Ti$_2$Ni, Ti$_4$Ni$_2$O	8000	1.12
350 ppm	Ti$_2$Ni	500	1.67

[0058] From the result of Table 1, the comparison sample which did not use a deoxidizer is understood that a maximum hydrogen storage capacity is as low as 1.12 (H/M). On the other hand, with the alloy of this invention, in spite of having used the vanadium system alloy raw material containing no less than 6000 ppm oxygen, it turns out that a high maximum hydrogen storage capacity comparable as the reference sample using a super-high-purity vanadium system alloy raw material with an oxygen content of 350 ppm can be demonstrated.

[0059] So that it may be set to example 2 alloy-composition V3TiNi0.56Nb0.047Ta0.047Co0.05M0.2 (M=Ca, Mg, or La) The weighing capacity of V as an alloy raw material, Ti, nickel and Nb, Ta and Co, CaNi5 as a deoxidizer, Mg2nickel, and the La is carried out, respectively, and it was made to be set to 60g on the whole. As a vanadium system alloy raw material, vanadium whose oxygen content is 5000 ppm was used. This vanadium is obtained from the refined vanadium oxide powder by the thermite reduction by the end of

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aluminium powder.

[0060] First, arc melting of these alloy raw material was carried out under reduced pressure argon atmosphere, and the casting alloy was produced. It carried out by less than output 50W, and the dissolution of a high-melting point alloy and the whole mixing were performed the early stages of arc melting. CaNi5, Mg2nickel, or La was put into this, and it dissolved in it. Then, after once cooling the molten metal and reversing the obtained alloy lump, the process of dissolving again was repeated several times. Alloy composition was uniformed, while this dissolution was performed by output 200-500W, and oxygen in an alloy reacted with Ca, Mg, or La in this process, forming the oxide and discharging these oxides out of the alloy.

[0061] In addition, the thing of the same alloy composition was produced like the above as a comparison sample except not using a deoxidizer. Furthermore, the thing of the same alloy composition was produced like the above except not having used a deoxidizer and having used vanadium of super high purity (oxygen content of 300 ppm) as a reference sample.

[0062] The organization etc. was analyzed about the obtained casting alloy. By X-ray fluorescence, Ca, Mg, and La of several percent were detected in the surface of the casting alloy of this invention, respectively. When the cross section of this alloy was analyzed by SEM-EPMA, the host phase of a vanadium solid solution and the TiNi set phase which deposited to that grain boundary were seen. Moreover, 0.5-1at.% grade detection of Mg and Ca was carried out at any phase. With the alloy which added La, a little La-nickel phases were observed from the cross section, and La of about 1 at.% was detected in the TiNi phase.

[0063] Subsequently, after carrying out hydrogenation grinding and carrying out disintegration of this alloy, when what carried out dehydrogenation at 500 degrees C among the vacuum was analyzed by X-ray diffraction analysis, the peak of the solid solution (bcc) of vanadium and the peak of the TiNi set phase were accepted. It was a result also with reference sample same about these. On the other hand, by the comparison sample, since a deoxidizer was not used, the difference on an organization was accepted. That is, although the host phase was a vanadium solid solution, the Ti4nickel2O phase besides a TiNi set phase and the vanadium solid solution phase whose Ti concentration is higher than a host phase were checked in the grain boundary.

[0064] After hydrogenating each alloy, copper powder was mixed to what carried out machine grinding, press molding of this was carried out, and the hydrogen storing metal alloy electrode was produced. This electrode was used as the negative electrode and the service capacity of the hydrogen storing metal alloy electrode was measured using carbonyl nickel in the positive electrode, using the KOH aqueous solution of 6M as an electrolyte. The discharging current density of measurement was set to 50Akg-1 or 200Akg-1 per alloy. Moreover, it carried out by having repeated charge and discharge, and the endurance over this cycle was investigated. The result is shown in Table 2. In addition, the oxygen concentration in an alloy of the obtained alloy is also collectively shown in Table 2.

[0065]

[Table 2]

表2

実施例2

脱酸剤	V内酸素濃度(ppm)	合金内酸素濃度(ppm)	C_d(50Akg^{-1})(Ahkg^{-1})	C_d(200Akg^{-1})(Ahkg^{-1})	100 C_{100}/C_d (%)
CaNi₅	5000	1200	360	210	86
Mg₂Ni	5000	1500	350	200	83
La	5000	800	360	220	84

参考資料・比較試料

脱酸剤	V内酸素濃度(ppm)	合金内酸素濃度(ppm)	C_d(50Akg^{-1})(Ahkg^{-1})	C_d(200Akg^{-1})(Ahkg^{-1})	100 C_{100}/C_d (%)
なし	300	600	360	200	88
なし	5000	7000	210	130	87

[0066] By a comparison sample, since the oxygen content is high, buildup of a hydrogen storage capacity cannot be aimed at, but the result of Table 2 shows that service capacity is also low. On the other hand, in the hydrogen storing metal alloy by the manufacture method of this invention, it turns out that the outstanding service capacity and endurance comparable as the reference sample which used super-high-purity vanadium can be demonstrated.

[0067] The same alloy V3TiNi0.56Nb0.047Ta0.047Co0.05 as example 3 example 2 was produced like the example 2. However, alloy V3TiNi0.56Nb0.047Ta0.047Co0.05 (alloy raw material A) and alloy V3TiNb0.047Ta0.047Co0.05 (alloy raw material B) were used as an alloy raw material.

[0068] The weighing capacity of V, Ti, nickel and Nb, Ta, and the Co was carried out first, the heating dissolution was carried out with the arc process, and the alloy raw material A and the alloy raw material B were produced. In this case, the thing with an oxygen content of 3000 ppm was used as vanadium. The oxygen concentration (oxygen concentration in an intermediate alloy) of the whole alloy raw material was 5000-6000 ppm.

[0069] Subsequently, Mg, Ca, or Mm (Mm: mixture of rare earth elements) is used for the alloy raw material A as a deoxidizer. CaNi5, Mg2nickel, or MmNi5 is added to the alloy raw material B as a deoxidizer. It prepared so that it might be set to V3TiNb0.047Ta0.047Co0.05 (CaNi5) 0.114, V3TiNb0.047Ta0.047Co0.05(Mg2nickel) 0.57, and V3TiNb0.047Ta0.047 (MmNi5) 0.114, respectively. Deoxidizers Mg, Ca, and Mm, CaNi5, Mg2nickel, or MmNi5 was put into the bottom of a water-cooled copper mold, and six kinds of alloy V3TiNi0.56Nb0.047Ta0.047Co(es)0.05 were produced by adding and carrying out arc melting of the rough alloy which dissolved beforehand and was alloyed from it. The alloy and the deoxidizer were mixed by carrying out by less than output 50W the early stages of arc melting.

[0070] Next, the alloy was reversed and remelted. Remelting was performed with the output of 200-500W, oxygen in an alloy reacted with Ca, Mg, or Mm in this process, and while discharging the oxide out of the alloy system, equalization of the alloy organization was attained.

[0071] When Ca, Mg, Mm, CaNi5, Mg2nickel, or MmNi5 was added and ingoted at the time of production of an

alloy, the following casting alloys were obtained. That is, in the casting alloy surface immediately after casting, Ca of several percent, Mg, or Mm was detected by X-ray fluorescence, respectively. Moreover, when the cross section of this alloy was analyzed by SEM-EPMA, in the host phase of a vanadium solid solution, the TiNi phase which deposited to that grain boundary was accepted. Moreover, 0.5-1at.% grade detection of Mg, Ca, and the Mm was carried out at any phase.

[0072] After carrying out hydrogenation grinding and making each alloy powdered, when what carried out dehydrogenation in the 500-degree C vacuum was analyzed by X-ray diffraction, the peak of a vanadium solid solution (bcc) and the peak of the TiNi set phase were seen. In this point, it was the same as that of the organization of the example of reference of an example 2. On the other hand, the difference in an organization was accepted with the alloy which did not add a deoxidizer using vanadium of high oxygen concentration. That is, although the host phase was a vanadium solid solution, a Ti4nickel2O phase and the vanadium solid solution phase whose Ti concentration is higher than a host phase other than a TiNi set phase were seen in the grain boundary.

[0073] Copper powder was mixed to what carried out machine grinding after hydrogenating six kinds of each alloy, press forming of this was carried out, and the hydrogen storing metal alloy electrode was produced. The KOH aqueous solution of 6M was used for carbonyl nickel and an electrolyte for this electrode, and the service capacity of the hydrogen storing metal alloy electrode was measured. The discharging current density of measurement was set to 50Akg-1 or 200Akg-1 per alloy. Moreover, it carried out by having repeated charge and discharge, and the endurance over this cycle was investigated. These results are shown in Table 3 with the oxygen concentration in an intermediate alloy, and the oxygen concentration in an alloy.

[0074]

[Table 3]
表 3

实施例 3

脱酸剂	中間合金内酸素濃度(ppm)	合金内酸素濃度(ppm)	C_1(50Akg^{-1}) (Ahkg^{-1})	C_1(200Akg^{-1}) (Ahkg^{-1})	100 C_{100}/C_1 (%)
Ca	5000	1000	320	170	88
Mg	5000	1200	300	170	84
Mm	5000	900	380	180	83
CaNi₅	6000	800	380	200	84
Mg₂Ni	5000	600	390	210	78
MmNi₅	5000	900	370	200	82

[0075] The result of Table 3 shows demonstrating the outstanding electrode characteristic comparable as an example 2 reference sample, in spite of having used the vanadium system alloy raw material of high oxygen concentration for the hydrogen storing metal alloy by the manufacture method of this invention.

[0076] Example 4V3TiNi0.56Hf0.24 is an alloy which has the three-dimensions network frame which becomes main [the Ti-nickel-V system AB2 type Laves phase] as the 2nd phase. What carried out the weighing capacity of V, Ti, nickel, Hf and CaNi5, Mg2nickel, or MmNi5 so that it might become the presentation of alloy V3TiNi0.56Hf0.24M0.2 (M=Ca, Mg, Mm), and was 60g on the whole was prepared. As vanadium, that whose oxygen content is 5000 ppm was used. This vanadium is the usual alloy which obtained it by having carried out thermite reduction of the refined vanadium oxide powder. That is, since it was not the super-high-purity article which performed electron beam refining under high vacuum atmosphere, it ended with low cost. And since it

ground easily because of dissolution oxygen, the handling of the weighing capacity of an alloy etc. was also easy.

[0077] Subsequently, these alloy raw material was dissolved and it alloyed. CaNi5, Mg2nickel, or MmNi5 was first put into the bottom of a water-cooled copper mold, and the rough alloy which dissolved on it was put in.

[0078] Arc melting of this was carried out under the bottom argon atmosphere of a reduced pressure, and the casting alloy was produced. In early stages, the output of arc melting was made less than 50W, and performed the dissolution of a refractory metal and the whole mixing. Subsequently, once cooling a molten metal, after reversing the obtained alloy lump and cooling, the process dissolved again was repeated several times. This dissolution was performed with the output of 200-500W, and alloy composition was uniformed, while oxygen in an alloy reacted with Ca, Mg, or Mm in this process and it was discharged out of the alloy system as an oxide.

[0079] In addition, the thing of the same alloy composition was produced like the above as a comparison sample except not using a deoxidizer. Furthermore, the thing of the same alloy composition was produced like the above except not having used a deoxidizer and having used vanadium of super high purity (the amount of oxygen of 350 ppm) as a reference sample.

[0080] The organization etc. was analyzed about the obtained casting alloy. By X-ray fluorescence, Ca, Mg, and Mm of several percent were detected in the surface of the casting alloy of this invention, respectively. Moreover, when the cross section of this alloy was analyzed by SEM-EPMA, the host phase of a vanadium solid solution and the Ti-nickel-V machine Laves phase which deposited to that grain boundary were seen. Moreover, 0.5-1at.% grade detection of Mg and Ca was carried out at both of the phases. About Mm, it was not detected in the host phase but about 1 at.% detection of was done into the Laves phase.

[0081] After carrying out hydrogenation grinding and making each alloy powdered, when what carried out dehydrogenation at 500 degrees C among the vacuum was analyzed by X-ray diffraction analysis, the peak of the Ti2nickel machine phase was accepted by the peak of the solid solution (bcc) of vanadium, the peak of a Laves phase, and still weaker hardness. About these, the same might be said of the case of a reference sample. On the other hand, by the comparison sample, since a deoxidizer was not used, the difference on an organization was seen. That is, although the host phase was the solid solution of vanadium, HfO_2 phase and Ti4nickel2O phase other than a TiNi set phase were accepted in the grain boundary.

[0082] After hydrogenating each alloy, machine grinding was carried out, subsequently copper powder was mixed, press molding of this end of mixed powder was carried out, and the hydrogen storing metal alloy electrode was produced. This electrode was used as the negative electrode, the KOH aqueous solution of 6M was used for the electrolyte, using carbonyl nickel as a positive electrode, and the service capacity of the hydrogen storing metal alloy electrode was measured. The discharging current density of measurement was set to 50Akg-1 or 200Akg-1 per alloy. Moreover, it carried out by having repeated charge and discharge, and the endurance over this cycle was investigated. The result is shown in Table 4.

[0083]

[Table 4]

表 4

実施例 4

脱酸剤	V内酸素濃度(ppm)	合金内酸素濃度(ppm)	C_1(50Akg^{-1})(Ahkg^{-1})	C_1(200Akg^{-1})(Ahkg^{-1})	100 C_{100}/C_1 (%)
CaNi₅	5000	1300	330	260	70
Mg₂Ni	5000	1000	330	240	64
MmNi₅	5000	900	340	240	74

参考資料・比較試料

脱酸剤	V内酸素濃度(ppm)	合金内酸素濃度(ppm)	C_1(50Akg^{-1})(Ahkg^{-1})	C_1(200Akg^{-1})(Ahkg^{-1})	100 C_{100}/C_1 (%)
なし	350	290	350	290	72
なし	5000	7000	135	40	92

[0084] By a comparison sample, since the oxygen content is high, improvement in a hydrogen storage capacity cannot be performed, but the result of Table 4 shows that service capacity is also low. On the other hand, in this invention article, it turns out that the outstanding service capacity and endurance comparable as the reference sample which used super-high-purity vanadium can be demonstrated.

[0085] Example 5 alloy V4TiNi0.65Co0.05Nb0.047Ta0.047 was produced.

[0086] The weighing capacity of CaNi5 or the Mg2nickel is carried out to the alloy raw materials V and Ti, nickel and Nb, Ta and Co, and a pan as a deoxidizer, respectively, and it was made to be set to V4TiNi0.65Co0.05Nb0.047Ta0.047M0.029 (M=Ca, Mg). As vanadium, the oxygen content used the super-high-purity article of 200 ppm or less.

[0087] CaNi5 or Mg2nickel of the deoxidizer was first put in in the water-cooled copper mold, the alloy raw material was paid on it at the low order of the fusing point, and arc melting was carried out under argon atmosphere. In addition, the thing of the same presentation was produced similarly [the above] as a comparison sample except not adding CaNi5 and Mg2nickel.

[0088] When the cross section of the casting alloy of this invention was analyzed by SEM-EPMA, the host phase of a vanadium solid solution and the TiNi phase which deposited to the grain boundary were seen. Moreover, about 0.5 at(s).% detection of Mg and Ca was done at the vanadium solid solution phase. This alloy was made to hydrogenate under a hot hydrogen atmosphere, and hydrogenation grinding of the casting alloy lump was carried out by cooling to a room temperature as it is.

[0089] It was checked that crystal structure has two bcc configurations by the vanadium solid solution and a TiNi set phase about every alloy. Most grating constants of the host phase were not changing. Moreover, change was not looked at by fine structure, either. In addition, those in which, as for the oxygen content in an alloy, the comparison sample added 600 ppm, CaNi5, and Mg2nickel were 500 ppm and 400 ppm, respectively.

[0090] The equilibrium pressure-presentation isothermal curve (PCT curve) about each alloy is shown in drawing 1 . By the comparison sample, the alloy which added 0.63 and CaNi5 is 0.64 with 0.66 and a Mg2nickel addition alloy, and the bleedoff hydrogen quantity (H/M) in 3.3-0.01MPa of 293K of each alloy became the highest value. This is because Ca dissolved to the host phase, and also is considered to be

because for dissolution oxygen in an alloy to have been returned by Ca at the time of an ingot. It is expected that service capacity becomes a big value from such a PCT curve.

[0091] After mixing with the copper powder of one 3 times the mass of this what carried out machine grinding of each alloy at the grain size of 75 micrometers or less, what carried out tablet molding by molding pressure 7.5 t/cm2 was used as the electrode. As activation characteristics of this electrode, change of the service capacity in the charge-and-discharge cycle of 10 cycles was investigated by discharging current density id=25Akg-1 (mAg-1) (drawing 2). Then, the high discharge characteristic was investigated by id=40-400Akg-1 (drawing 3), and succeedingly, by id=25Akg-1, the charge-and-discharge cycle examination was done and it investigated about endurance (drawing 4). in addition, a reference pole -- Hg-HgO set 5h and cutoff electric potential to 293K, and measurement temperature carried out charge by -0.75Vvs.Hg-HgO by 100Akg-1.

[0092] Activation characteristics became 76% or more of capacity of the highest service capacity by 1 cycle eye, as shown in drawing 2 , and they showed the standup which was excellent in every alloy. With the alloy which added CaNi5, it became the service capacity of 361Akg-1 high about 10% as compared with the comparison sample. Improvement in performance was found also what added Mg2nickel.

[0093] At high ******, as shown in drawing 3 , service capacity improved by id<=200Akg-1 by addition of CaNi5 and Mg2nickel. When CaNi5 was added, the service capacity of 220Akg-1 was obtained by id=200Akg-1. The improvement in performance with the same said of the case of Mg2nickel addition was accepted.

[0094] Moreover, also about the charge-and-discharge cycle characteristic, as shown in drawing 4 , any alloy was good.

[0095] As shown in drawing 1 - drawing 4 , when not only the thing for which the vanadium system raw material of the inexpensive amount of high oxygen can be used effectively but also the vanadium system alloy raw material of super high purity (the amount of hypoxia) is used, by the manufacture method of this invention, it turns out that more excellent characteristics are acquired.

[Translation done.]